Generating Trace Moisture with Dilution Techniques

Recent work at NIST has focused on extending primary trace humidity standards to moisture concentrations less than one part per billion (ppb, or nmol/mol). Our customers are 1) semiconductor process gas suppliers, who are under increasing pressure to deliver process gasses with water contamination levels approaching 1 nmol/mol or less, and 2) hygrometer manufacturers, who need sub-nmol/mol humidity standards in support of emerging hygrometer technologies. Commercial hygrometers that support semiconductor processing are now capable of measuring moisture concentrations of 0.1 nmol/mol, but there have not been any methods of reliably generating such low concentrations. Currently, NIST is the world leader in trace humidity, and is the only NMI that has the capability of picomol/mol trace humidity generation that is tied to fundamental physical properties.

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The NIST Low Frost-Point Generator (LFPG) provides a source of nitrogen gas with moisture concentrations as low as 10 nmol/mol. Commercialized advances in flow metrology make accurate flow metering possible, and enable construction of a divided-flow humidity generator that combines the gas stream from the LFPG with a second, accurately metered flow of dry diluent gas. The primary technical challenge is to perform the flow measurements, combine the gas stream, and deliver the gas stream to the test instrument without introducing excess moisture from desorption of water from tube walls or other sources.

Following construction of the dilution apparatus, we first demonstrated that the dilution technique produced moisture concentrations in agreement with those produced directly from the LFPG. We then successfully extended the lower limit of the moisture concentration to 0.4 nmol/mol by the dilution method.

Our measurements revealed that further improvements are limited not by the dilution scheme itself, but by limitations in our understanding of adsorption/desorption of water from the walls of the apparatus. The performance of the dilution apparatus depends critically on having a source of diluent gas that is sufficiently dry. To test the adequacy of our commercial gas dryer, we developed a liquid-argon cold trap that provides a thermodynamically based method of generating dry gas of ultra-low moisture concentration. Comparison of gas from our commercial dryer with that passed through the cold trap revealed no measurable difference in moisture concentration.

Impact: Our recent dilution tests were the first quantitative tests of commercial hygrometers at this concentration range with gas streams of known concentration. The three leading US manufacturers of optical systems for trace moisture generation have all had instruments tested against the LFPG in the past. With the extension of the range of the LFPG, we anticipate further testing down to the lower limits of these instruments.

Future Plans:
We have acquired an optical hygrometer capable of 0.1 nmol/mol resolution that will enable us to conduct quantitative studies of water desorption from the walls of gas manifolds and related plumbing. Several industrial manufacturers of tubing and valves will be collaborating with us by supplying materials that promise ultra-low water desorption.